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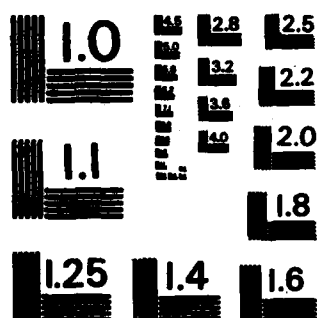
FLUORESCENCE DETECTED SURFACE EXAFS (FDSEXAFS) OF  
IODINE ON PLATINUM: AN. (U) PUERTO RICO UNIV RIO  
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ON PLATINUM: IN-SITU STRUCTURAL  
CHARACTERIZATION OF AN ELECTROCHEMICAL INTERFACE

By

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**ABSTRACT:**

Using grazing incidence geometry and fluorescence detection, surface EXAFS of iodine adsorbed on platinum (111) single crystals has been observed. Fourier analysis of the data yields a Pt-I distance of 2.46 Å. These results demonstrate the feasibility of employing SEXAFS for the in-situ structural study of electrochemical interfaces.

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The structure of the electrode/solution interface represents a problem of fundamental importance in electrochemistry and other interfacial disciplines since its properties greatly affect reactivity. (1) This problem has, until recently, proved very elusive to experimental study. Indeed, most of our knowledge of the structure of the electrochemical interface is based on indirect evidence which relies primarily on theoretical models to explain kinetic, thermodynamic or spectroscopic data. (2-5) In recent years, however, the study of the solid/electrolyte interface has received renewed attention (6) due, in part, to the development of new spectroscopic techniques such as surface enhanced raman spectroscopy (SERS) (7) electrochemically modulated infra red reflectance spectroscopy (EMIRS) and related techniques (8) which give information about the identity and orientation of interfacial species. These techniques, however, do not reveal the structure or geometric arrangement of species at the interface. Hence, in spite of its importance, our knowledge of the structure of electrochemical interfaces at the atomic or molecular level is still quite limited. This can be attributed in part to the lack of structure sensitive techniques that can operate in the presence of a condensed phase. Ultra high vacuum (UHV) surface spectroscopic techniques such as low energy electron diffraction (LEED) Auger electron spectroscopy (AES) and others have been applied to the study of electrochemical interfaces, and a wealth of information has emerged from these ex-situ studies. (4,9-12) However, the fact

that these techniques require the use of UHV, precludes their use for in-situ studies of the electrode/solution interface and transfer of the electrode from the electrolytic medium into UHV introduces the very serious question of whether the nature of the surface examined ex-situ has the same structure as the surface in contact with the electrolyte and under potential control.

The advent of synchrotron radiation (13) has dramatically changed the outlook. Both XANES (x-ray absorption near edge structure) and EXAFS (extended x-ray absorption fine structure) (14) can, in principle, be applied in-situ to the study of the electrode/electrolyte interfaces. These techniques can be used to obtain information concerning the oxidation state of interfacial species as well as structural information on site symmetry, chemical bonding, interatomic distances and the coordination number about a species in an adsorbed layer while the electrode is under potential control.

Recent experiments have demonstrated the utility of surface EXAFS for studying the structure of monolayers of adsorbed atoms on solid surfaces. (15) Of particular interest is the use of fluorescence detection surface EXAFS (FDSEXAFS) (16,17) since it can be applied to systems in contact with fluid phases. Recent studies by Kordesch and Hoffman (12) have demonstrated that in-situ FD EXAFS can be performed on electrochemical systems. Heald, Keller and Stone (16) have demonstrated that monolayer sensitivity is possible.

In a previous experiment (18), we attempted to measure the structure of monoatomic layers of bromine and lead on an epitaxially deposited silver (111) single crystal (on a mica support) and although a clear absorption edge was detected, the signal was too noisy for use in the determination of structural parameters.

For the experiment reported here, we have employed a very small angle of incidence (grazing), as originally suggested by Stern (19) et. al. This approach is attractive because it eliminates most of the background scattering due to the electrode. However, the effective pathlength of the x-ray beam through the electrolyte is greatly amplified (by a factor of about 300) so thin layers of solution need to be employed.

We describe here our observation of FDSEXAFS from a monolayer of iodine adsorbed onto platinum (111) single crystal electrodes. Although the adsorption in this system is irreversible and the experiments were not done under potential control, the results presented clearly establish the utility of this technique for the in-situ study of the electrode/solution interface.

#### Experimental:

Experiments were performed in the A-2 station (wiggler line) of the Cornell High Energy Synchrotron Source (CHESS) facility.

Samples were mounted on a rotatable lexan holder inside a rectangular lexan cell provided with mylar windows. The cell



could be filled with electrolyte solution so that partial or total immersion of the electrode could be achieved. The sample holder itself was connected to a goniometer which allowed rotation of the sample with low resolution over  $360^\circ$  and high resolution over about 10 degrees of arc. We feel that this cell assembly has many advantages over that recently reported by Kordesch and Hoffman.(12)

The platinum single crystals were grown from the melt at the materials preparation facility of the Cornell University's Materials Science Center. After cutting and polishing, the samples were cleaned by argon sputtering and subsequently exposed to iodine vapor. According to Hubbard and coworkers (20), this procedure eliminates most of the carbon and oxygen contamination from the surface and furthermore the strongly chemisorbed layer of iodine on the surface minimizes subsequent contamination of the surface.

X-ray fluorescence was detected with a high purity germanium detector (GLP 363360/13; EG&G ORTEC) used in conjunction with an ORTEC model 673 spectroscopy amplifier and a model 551 timing single channel analyzer. An ionization chamber was used to monitor the incident intensity. Lead sollar slits and antimony film filters (deposited on beryllium foils) were used to minimize scattered radiation.

[Pt(acac)<sub>2</sub>I<sub>2</sub>] (acac is acetylacetonate) was used as the reference material (or "model compound") for determining the appropriate phase shifts. It was synthesized and purified

according to the procedure of Dahl and coworkers.(21) Five spectra for the model compound were averaged to obtain a composite spectrum. The XOPLUS data collection program (CHESS) was used to obtain the raw spectra, while all further data reduction and processing were performed by modified versions of the EXAFS analysis program of B. Kincaid (AT&T Bell Labs.) and the calculations were performed on Prime or PDP-11 computers.

#### Results and Discussion:

The first series of experiments were performed using an angle of incidence of  $45^\circ$ . However, the background scatter was of such a magnitude that though an edge was observed, the signal-to-noise was not sufficient for structural analysis.

At this point we changed to the grazing incidence configuration. Under these experimental conditions, the signal-to-noise ratio was improved by at least an order of magnitude over the  $45^\circ$  results. In fact, a good signal to noise ratio was obtained even when the electrode was covered by a thin film of electrolyte.

Figure 1 shows the average of three runs using a platinum (111) single crystal with adsorbed iodine. There is a very well defined K absorption edge and although the EXAFS region is somewhat noisy, there is clearly structure present.

Figures 2 A and B show the background subtracted spectra in k space prior to and after filtering, respectively.

Fourier analysis of the data showed a dominant peak (Figure

3) from which we obtained a Pt-I distance of 2.46 Å. Phase shifts were obtained from the spectrum of  $[\text{Pt}(\text{acac})_2\text{I}_2]$ . Note that because of the polarization of the incident x-ray beam, we are relatively insensitive to I-I scattering. Possible multiple scattering effects were also ignored. Analysis of the spectra using the phase shifts computed by Teo and Lee (22) yielded shorter distances. Reported Pt-I distances range from 2.6 to 3.0 Å.

These discrepancies aside, these studies demonstrate that FDSEXAFS can yield structural information of adsorbed monolayers at a metal/liquid interface and we are confident that further improvements in the experimental technique will make this a very powerful in-situ structural probe for the study of solid/liquid interfaces.

Although the specific case studied represented an irreversible adsorption, we are now pursuing the study of systems that exhibit reversible adsorption or deposition; with particular emphasis being placed on systems that undergo underpotential deposition. We hope to perform in-situ studies of the potential dependence of the structural changes that take place as a material is deposited on an electrode surface.

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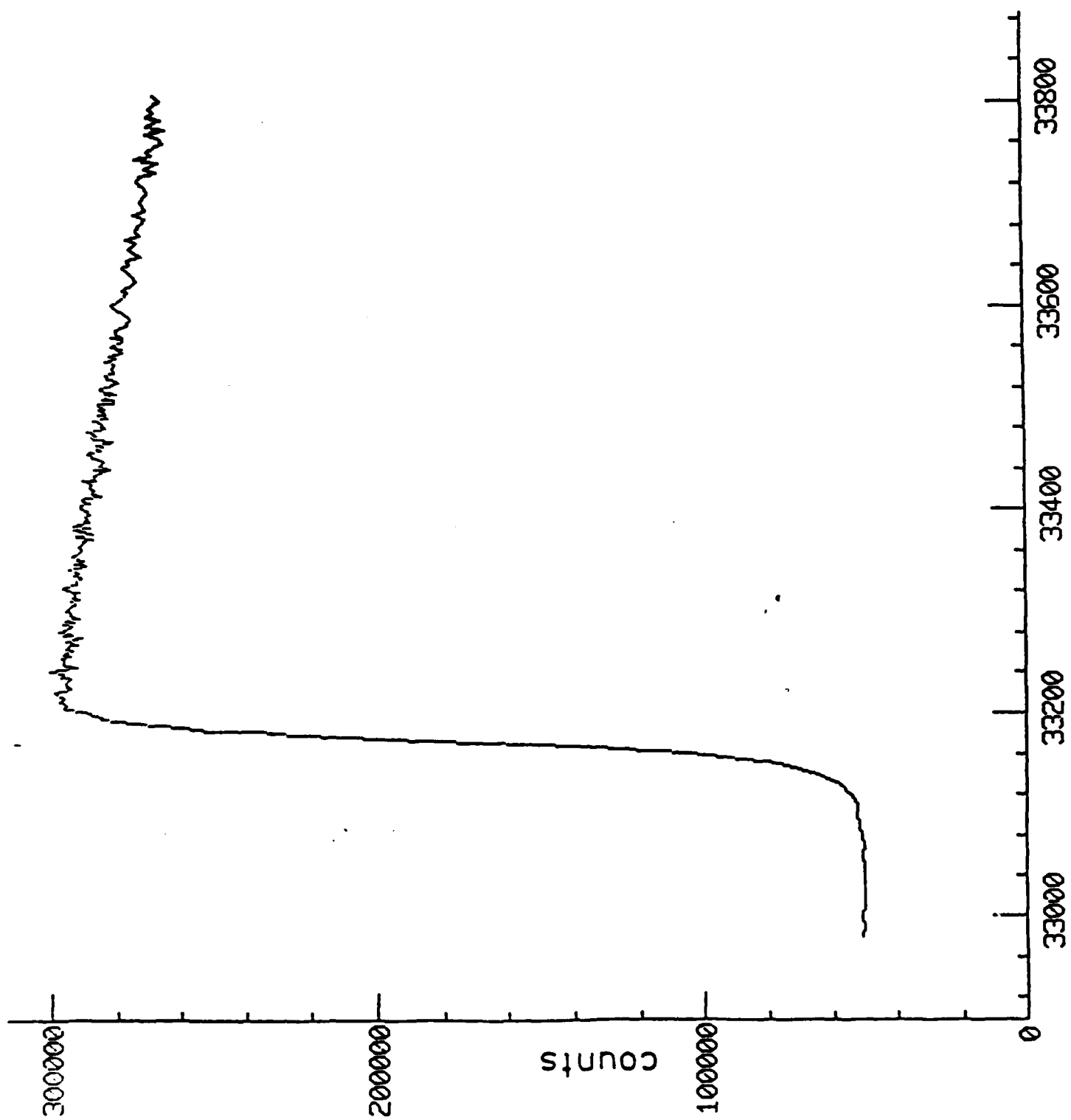
We are very grateful to Dr. Brian M. Kincaid (AT&T Bell Labs) for his advice and for providing us with a copy of his EXAFS data analysis program.

**Figure Legends:**

**Figure 1.** Composite EXAFS spectrum (average of three runs) for iodine adsorbed on a Pt (111) single crystal.

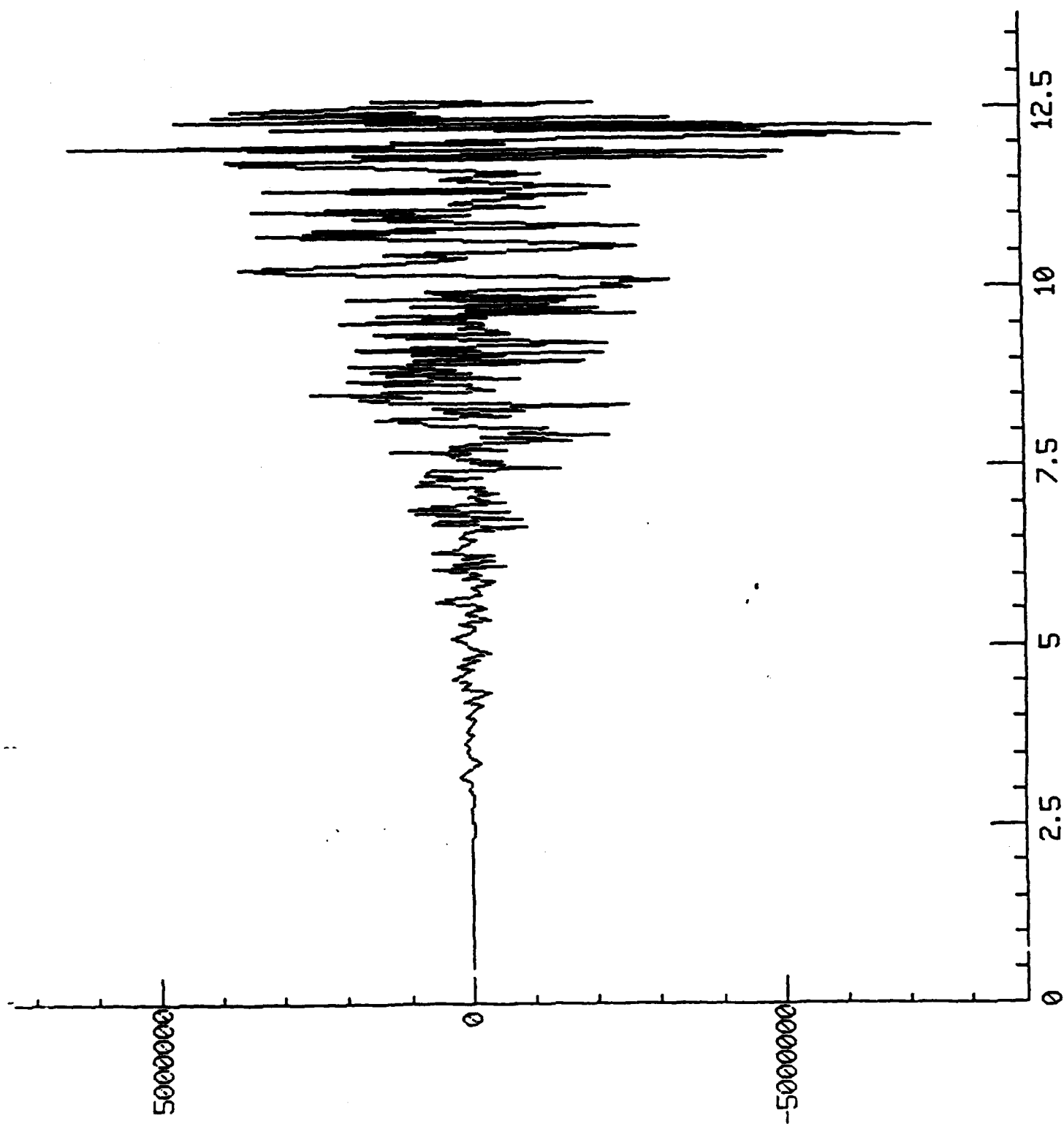
**Figure 2.** Background subtracted spectra in  $k$  space before (A) and after (B) filtering.

**Figure 3.** Fourier Transform of spectrum in  $k$  space into the radial distribution function vs. distance.



Gamma





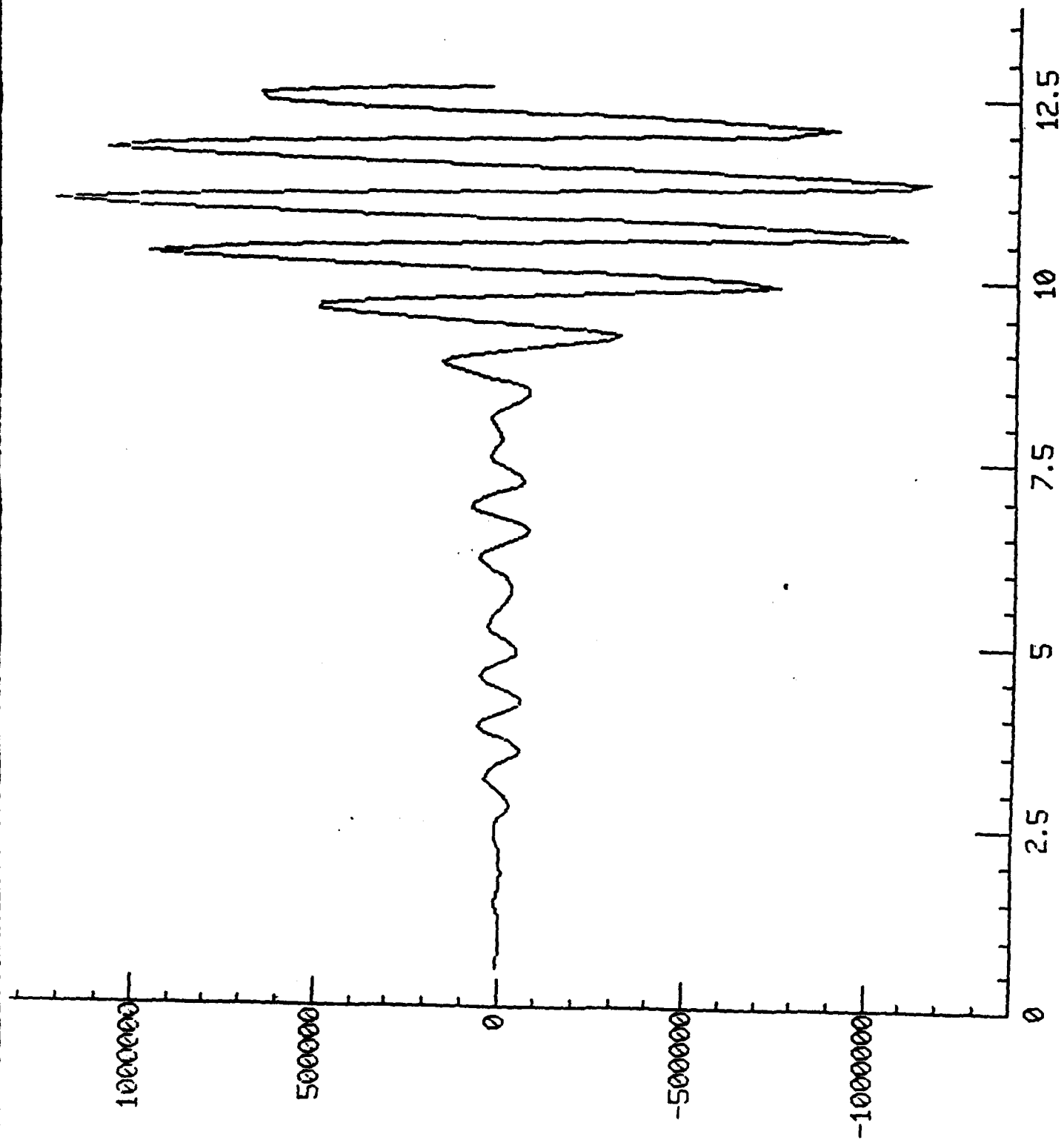
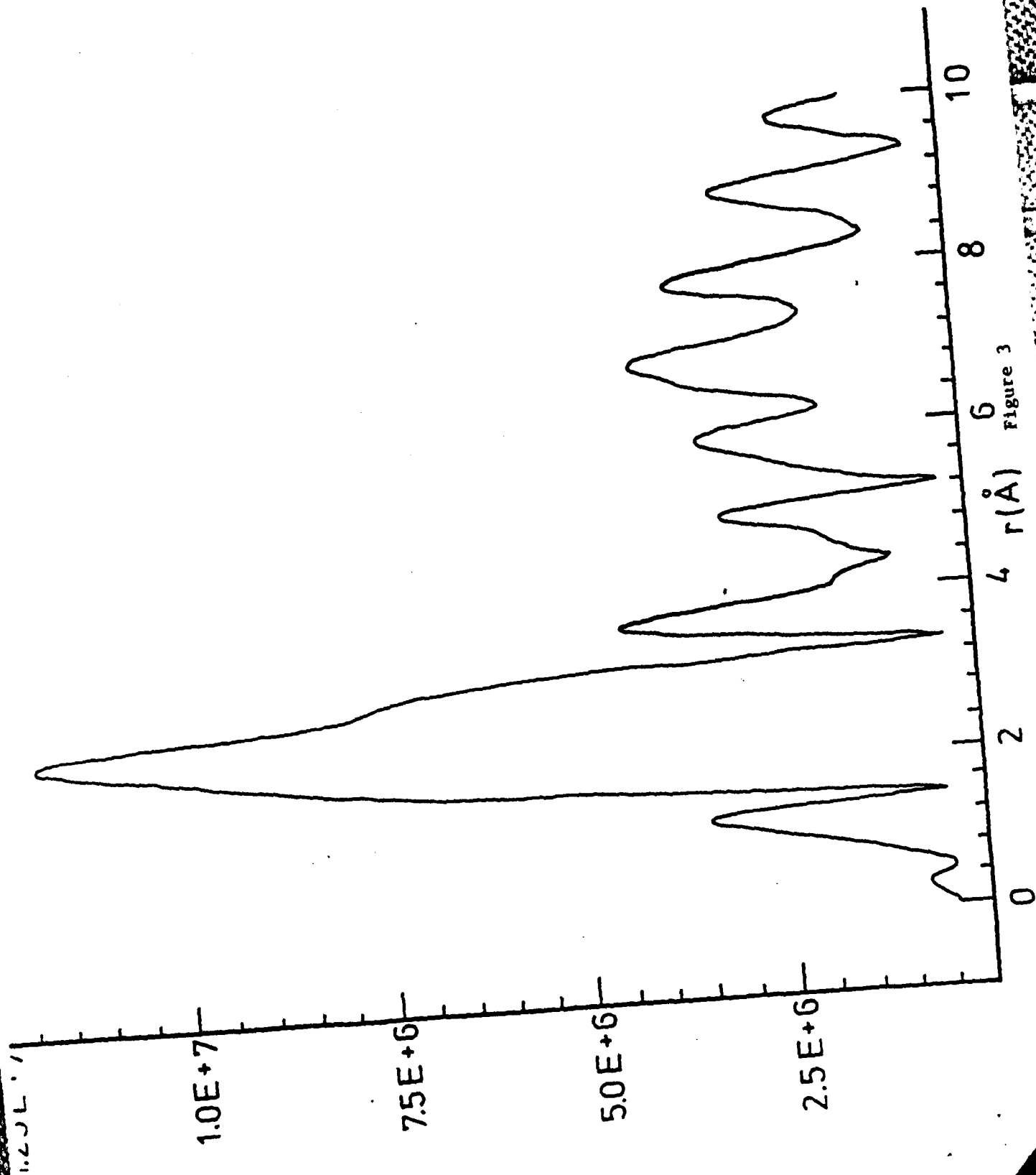


Figure 2B



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